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THE INTERACTION OF HYDROGEN ION WITH TETRAMMINEPALLADIUM (II) ION IN THE PRESENCE OF NITRATE AND CHLORIDE IONS

JAMES R. FUNCK

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THE INTERACTION OF HYDROGEN ION WITH TETRAMMINEPALLADIUM (II) ION IN THE PRESENCE OF NITRATE AND CHLORIDE IONS

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James R. Funck

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THE INTERACTION OF HYDROGEN ION WITH TETRAMMINEPALLADIUM (II) ION IN THE PRESENCE OF NITRATE AND CHLORIDE IONS

by

James R. Funck II

Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

United States Naval Postgraduate School
Monterey, California

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James R. Funck

This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE

from the
United States Naval Postgraduate School

ABSTRACT

In acidic aqueous ammonium nitrate media, the rate law for the replacement of ammonia in tetramminepalladium (II) was found from pH measurements to be approximately

$$\frac{-d[H^+]}{dt} = \frac{3.7\,[Pd(NH_3)_4^{++}][H^+]}{sec.\ [X]} \text{ for the first replacement}$$

and

$$\frac{-d[H^+]}{dt} = \frac{7.0\,[Pd(NH_3)_3(Y)^{++}][H^+]}{sec.\ [X]} \text{ for the second replacement}$$

where: $X = NH_4^+$ or NO_3^-

$Y = H_2O$ or NO_3^-

Values of the equilibrium constants for

$$Pd(NH_3)_4^{++} + H^+ + Y \overset{K_1}{\rightleftharpoons} Pd(NH_3)_3(Y)^{++} + NH_4^+$$

and

$$Pd(NH_3)_3(Y)^{++} + H^+ + Y \overset{K_2}{\rightleftharpoons} Pd(NH_3)_2(Y)_2^{++} + NH_4^+$$

were found to be approximately 4.6×10^6 for K_1 and 2.6×10^4 for K_2 when Y was assumed to be water, and 2.4×10^7 for K_1 and 9.7×10^4 for K_2 when Y was assumed to be nitrate ion.

Absorption spectra showed peaks for $Pd(NH_3)_4Cl_2$ at 295 mμ (ϵ = 201) and for $Pd(NH_3)_2Cl_2$ at 370 mμ (ϵ = 178). In addition, all solutions containing a palladium-ammonia complex showed intense absorption at wave lengths below approximately 240 mμ.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor Richard A. Reinhardt of the U. S. Naval Postgraduate School in this investigation.

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TABLE OF SYMBOLS

$[H^+]_1$	The concentration that would have resulted from the total hydrogen ion in solution if no reaction occurred.
$[H^+]_2$	$[H^+]_1$ less the change in concentration resulting from the hydrogen ion required to neutralize the ammonia ($[H^+]_1 - [NH_3]_0$)
$[H^+]_3$	$[H^+]_2$ less the change in concentration resulting from the hydrogen ion required to complete the first step of the substitution in the reaction. ($[H^+]_2 - [Pd(NH_3)_4^{++}]_0$)
$[H^+]_4$	The last measured value of hydrogen ion concentration for a particular run.
C	Concentration in millimoles per liter.
*	Values graphically extrapolated to time of zero from plots of hydrogen ion versus time.
ϵ	Extinction coefficient
Y	Nitrate ion or water
X	Ammonium ion or nitrate ion

I. Introduction

Dichlorodiamminepalladium (II) can be prepared by the following series of reactions [11]

$$PdCl_2 + 2Cl^- = PdCl_4^{--} \quad (1)$$

$$2PdCl_4^{--} + 4NH_3 = Pd(NH_3)_4\ PdCl_4(s) + 4Cl^- \quad (2)$$

$$Pd(NH_3)_4PdCl_4(s) + 4NH_3 = 2Pd(NH_3)_4^{++} + 4Cl^- \quad (3)$$

$$Pd(NH_3)_4^{++} + 2H^+ + 2Cl^- = Pd(NH_3)_2\ Cl_2(s) + 2NH_4^+ \quad (4)$$

In a preliminary study, and under a limited range of conditions, Reinhardt [15] found that in the initial stages of the reaction (eq. 4) the rate was independent of the concentration of hydrogen ion. This observation aroused interest as to the nature of the kinetics of this reaction.

Dinitratodiamminepalladium (II) can be prepared in solution by replacing the chloride ion in equation 4 with nitrate ion [11].

Banerjea and Tripathi [8] reported on the rates of stepwise substitution of chloride and nitrate groups in trans-dichlorodiamminepalladium (II) and other similar palladium compounds by various reagents of differing nucleophilic character. The reactions, followed by conductance measurements, were found to be of the S_N2 type with the rates decreasing in approximately the same order as the nucleophilic character of the incoming groups. Most of the reactions were found to be very fast, with the majority reaching completion in less than one minute at 36°C.

Bassolo, Gray, and Pearson [9] reported a kinetic study of the replacement of a ligand Z in platinum (II) and palladium complexes of

the type $M(dien)Z^+$ and $M(tripy)Z^+$ by pyridine in aqueous solutions. These reactions were also followed by measuring changes in the electrical conductivity of the solutions. For the palladium complexes, when Z was a halogen, the calculated infinity value of conductivity was reached within 10 seconds at 25.1°C for most of the runs.

From studies on dichlorodiamminepalladium (II), Reinhardt reported [13] that the replacement of one of the chloride ions by water is a stepwise reaction.

Since these studies showed the reactions to be very fast, the proposed methods of analysis for this study were limited to rapid instrumental types which could be made directly on the reacting solution. The most promising types were potentiometric and spectrophotometric, with measurement of the pH of the solution as the favored method.

II. Experimental Procedure

Since the reactions (eq. 2 and 3) leading to the formation of tetramminepalladium (II) ion produce free chloride ions, some method was sought to eliminate the chloride ion at this point in the preparation. With this in mind, feasibility studies were made on a system to produce tetramminepalladium (II) nitrate. Drew, et al. [11] prepared this compound by the following reactions:

$$Pd(NH_3)_4PdCl_4 + 2AgNO_3 = Pd(NH_3)_4(NO_3)_2 + Ag_2PdCl_4 \quad (5)$$

$$Pd(NH_3)_4Cl_2 + 2AgNO_3 = Pd(NH_3)_4(NO_3)_2 + 2AgCl \quad (6)$$

However, to eliminate any complications produced by any silver ion remaining in solution when the chloride ion was added (eq. 4), it was decided to prepare $Pd(NH_3)_4(NO_3)_2$ by adding excess ammonia to $Pd(NO_3)_2$. When ammonia was added to $Pd(NO_3)_2$ dissolved in distilled water, an extremely fine brown precipitate formed, which was believed to be an oxide of palladium. Following removal of this precipitate, the solution was acidified with excess HCl and the reaction followed with a Zeromatic pH meter. The $Pd(NH_3)_2Cl_2$ desired was obtained and the pattern of the change in the hydrogen ion concentration agreed very well with that found in initial studies of the preparation of $Pd(NH_3)_2Cl_2$ by equations 2, 3 and 4. Therefore all of the following studies were conducted on the nitrate system.

A $Pd(NH_3)_4(NO_3)_2$ stock solution was prepared by dissolving five grams of $Pd(NO_3)_2$, obtained from Fisher Scientific Company, in 500 ml. of water. Then an excess of NH_3 was added, followed by gentle heating,

after which the solution was allowed to stand for an hour. After the solution was warmed, the fine brown precipitate formed. Nitric acid, which had been boiled to remove the NO_2, was then added in sufficient quantity to reduce the pH to 6.97 ± 0.02. The fine precipitate was then removed by first filtering through an asbestos mat with suction, followed by a second filtration after the filtrate had been mixed with some diatomaceous silica filter aid (Celite). The solution was diluted to 2000 ml. and then analyzed for palladium using dimethylglyoxime to precipitate the palladium.

The dimethylglyoxime (DMG) solution was prepared by dissolving 0.9 gram DMG in 99 ml. of 95% ethyl alcohol. To each 25 ml. aliquot of $Pd(NH_3)_4(NO_3)_2$ stock solution, 2 ml. of acetic acid and 25 ml. of the DMG solution were added. The resulting solution was then diluted to 300 ml., warmed gently and allowed to stand for at least one hour. The precipitate was filtered through a sintered glass crucible using suction. After testing the filtrate for incomplete precipitation, the precipitate was washed first with a one percent HCl solution and then cold water. The precipitate was then dried in an oven at 100°C for periods of one hour until constant weight was achieved. The masses of the precipitates, as determined on a Mettler type H-16 balance (accurate to ± 0.00002 grams) [16], were 0.02598 grams, 0.02600 grams and 0.02613 grams. An average value of 0.02604 grams was used in the calculation. The concentration of palladium in the stock solution, as determined by using 0.3167 as the theoretical factor, was 3.091×10^{-3} M.

The amount of NH_4NO_3 in the $Pd(NH_3)_4(NO_3)_2$ stock solution was determined by evaporating to dryness a 25 ml. sample of the solution and

weighing the residue. The masses of the residue were 1.57690 grams, 1.57691 grams and 1.57698 grams. An average value of 1.57693 grams was used in the calculation. The quantity of $Pd(NH_3)_4(NO_3)_2$, corresponding to the concentration of palladium determined above, was subtracted and the remainder was NH_4NO_3. Thus the NH_4NO_3 was 0.77639 M.

The nitric acid solutions used in the runs were titrated against a commercial brand (Hellige Certified Reagent) 0.1000 N sodium hydroxide solution.

All pH measurements were made with a Beckman model GS pH meter (Ser. #173486) with a general purpose external shielded glass electrode (#40498) and a fiber type external shielded calomel electrode (#39170). This instrument has a sensitivity and reproducibility of ±0.0025 pH units [17]. At 25.0°C the pH of the sample measured by the GS pH meter is calculated by

$$pH_s = pH_b + 0.003381(r_b - r_s) \tag{7}$$

where: pH_s = pH of sample

pH_b = pH of buffer

r_b = duodial reading for the buffer

r_s = duodial reading for the sample.

Prior to each run the model GS pH meter was calibrated with standard commercial buffers. Due to lack of availability of buffers and the pH range to be covered, various brands of buffers had to be used. The buffers used were:

a. pHydrion pH 3.00 (4.00) ± 0.05 @ 25.0°C

b. Beckman pH 7.02 ± 0.02 @ 20.0°C

pH 7.00 ± 0.02 @ 25.0°C

pH 6.97 ± 0.02 @ 40.0°C

c. Coleman pH 3.01 (4.01) ± 0.01 @ 25.0°C

pH 3.00 (4.00) ± 0.01 @ 30.0°C

All of the reactions were run in a small water bath using a Fisher electronic control relay and a Philadelphia microset thermostat, which held the temperature at 25.0°C ± 0.02. The stock solutions were kept in the same water bath. This reduced the time required for the solutions used in a run to attain the operating temperature, and also reduced to a minimum any errors in volumetric measurements.

The procedure for each run was as follows:

a. The model GS pH meter was turned on and allowed to warm up.

b. A 150 ml. beaker which had been cleaned, dried in an oven and placed in the water bath was partially filled with buffer solution.

c. The electrodes were rinsed with distilled water, dried with tissues and placed in the buffer solution.

d. The pH meter was read until a constant duodial reading for the buffer was obtained. This usually took 15-30 minutes.

e. The $Pd(NH_3)_4^{++}$ solution and sufficient water to make a total of 100 ml., less the amount of acid to be added later, were pipetted into another cleaned and dried 150 ml. beaker. The pipettes were rinsed three times with the solution to be measured prior to transferring the solution. Following every transfer the pipettes were allowed to drain for 20 seconds.

f. The electrodes were removed from the buffer solution, rinsed with distilled water, dried with tissues and placed in the solution from (e), which was now in the water bath.

g. The above solution was allowed to stand in the water bath about 15 minutes to insure that it was again at 25.0°C. During this time the acid solution was removed from the bath and the pipette rinsed.

h. The acid was then added and the electric clock started when the pipette bulb was approximately half empty.

i. The pipette was allowed to drain and the solution was stirred. By the time the pH meter could be balanced the earliest reading that could be made was one minute after starting the clock. The times of subsequent readings are shown in the tables in the appendix. The reaction solution was stirred manually by means of a curved glass stirring rod at least once between each reading for the first ten minutes and thereafter at frequent intervals during the remainder of the run.

In order to obtain a reasonable change in pH of the reaction solution, with the relatively low concentration of $Pd(NH_3)_4^{++}$, all but two runs were conducted with the initial concentration of hydrogen ion and $Pd(NH_3)_4^{++}$ of the same order of magnitude. The other two runs were conducted by isolation with the hydrogen ion as the limiting reactant.

The concentration of ammonia in the reaction solution was computed from the measured hydrogen ion concentration of the $Pd(NH_3)_4^{++}$ stock solution, using the equilibrium relation for

$$NH_3 + H^+ \rightleftharpoons NH_4^+ , \qquad K = 1.774 \times 10^9 \ [6] \tag{8}$$

Since the concentration of ammonium ion was already known, the ammonia concentration was easily determined. However the calculated ammonia concentration is extremely sensitive to a very small variation in the measured value of hydrogen ion concentration.

A limited number of runs were conducted on a Beckman model DU spectrophotometer. A hydrogen arc lamp and matched silica cells (path length of 1.000 cm.) were used to study absorbance in the range of 220-400 mμ. A calibration over the range concerned, showed the two cells to be matched within the reading accuracy of the instrument. Distilled water was always used in the reference cell. These runs were intended to provide information as to the rate of formation of $Pd(NH_3)_2Cl_2$ from absorbance measurements over a period of time.

III. Experimental Results

A. Absorption Spectra

The results of the experimental runs are:

a. A solution of 4.26 x 10^{-3} M $Pd(NH_3)_4^{++}$ prepared by equations 1, 2 and 3 showed absorbance ($\log \frac{I_o}{I}$) peaks of 0.990 at 295 mμ and an increasing absorbance at 220 mμ (curve A, fig. 1). 220 mμ is the lower limit of the model DU spectrophotometer. Babeaba [5] reported the major absorption peak of $Pd(NH_3)_4Cl_2$ dissolved in water as 294 mμ.

b. The solution from (a) was acidified with excess HCl and allowed to stand until $Pd(NH_3)_2Cl_2$ crystals appeared. Examination of the solution showed absorbance peaks of 0.987 at 390-395 mμ, 1.805 at 275 mμ and greater than 3.0 between 220 and 240 mμ (curve B, fig. 1).

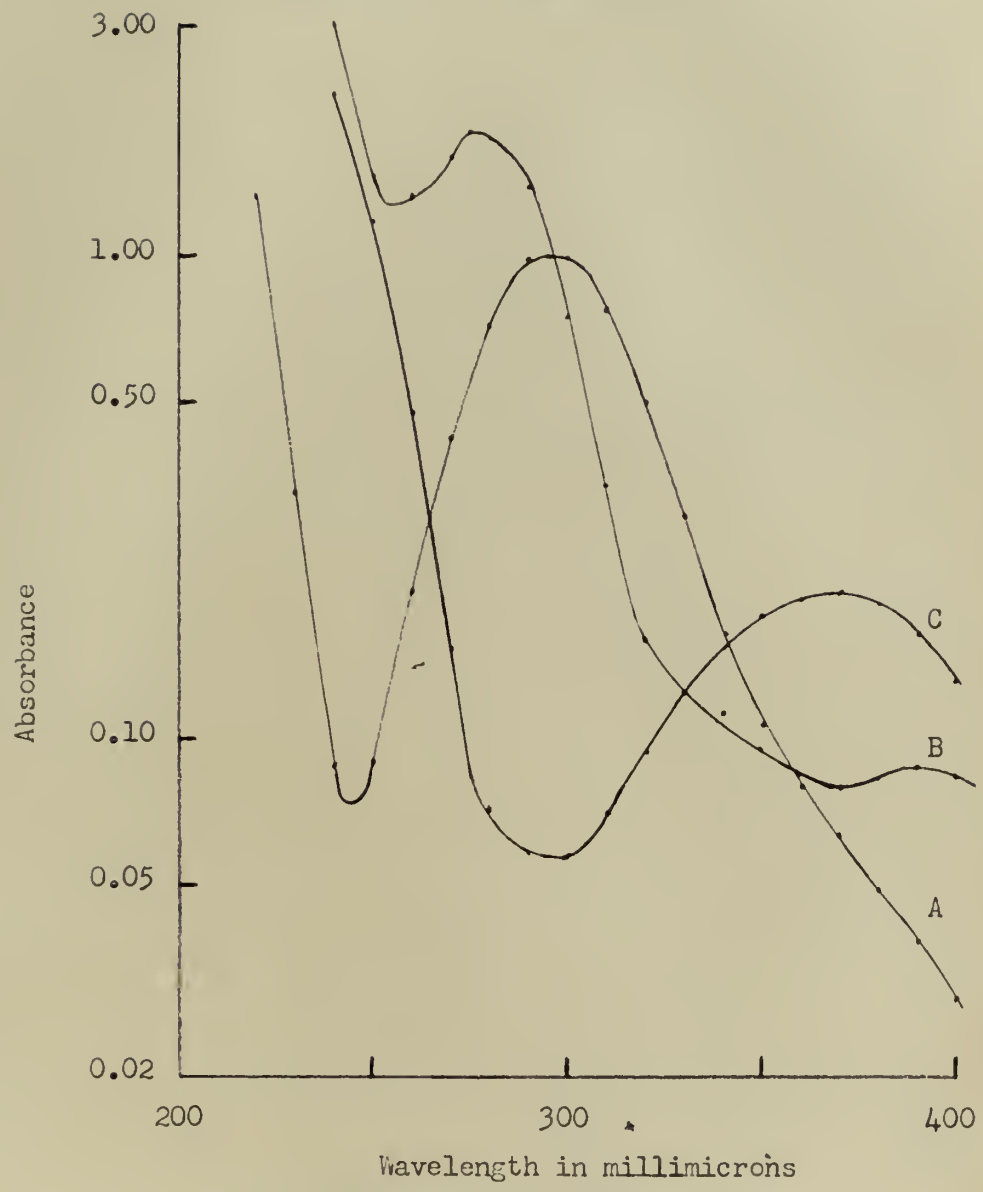
c. A saturated solution of $Pd(NH_3)_2Cl_2$ crystals dissolved in distilled water showed an absorbance peak of 0.200 at 370 mμ and greater than 3.0 between 220 and 235 mμ (curve C, fig. 1). Babeaba [5] reported the major absorption peak of $Pd(NH_3)_2Cl_2$ as 376-380 mμ.

d. A 9.867 x 10^{-2} N HNO_3 solution showed only the absorbance peak of 0.704 at 300 mμ, which can be attributed to the nitrate ion (curve B, fig. 2). The $Pd(NH_3)_4(NO_3)_2$ stock solution showed the extremely strong absorption peak of the nitrate ion and an absorbance greater than 3.0 below 245 mμ (curve A, fig. 2). These absorptions were sufficiently strong to screen the known peaks of $Pd(NH_3)_4Cl_2$ and $Pd(NH_3)_2Cl_2$ if these had been present.

The strong absorption below 250 mμ could not be associated with any particular species, but appeared whenever a palladium-ammonia compound, of one form or another, was present. Since these results indicated that this method was not feasible to determine the rate of production of $Pd(NH_3)_2Cl_2$, further studies were abandoned.

Figure 1

Absorbance vs Wavelength



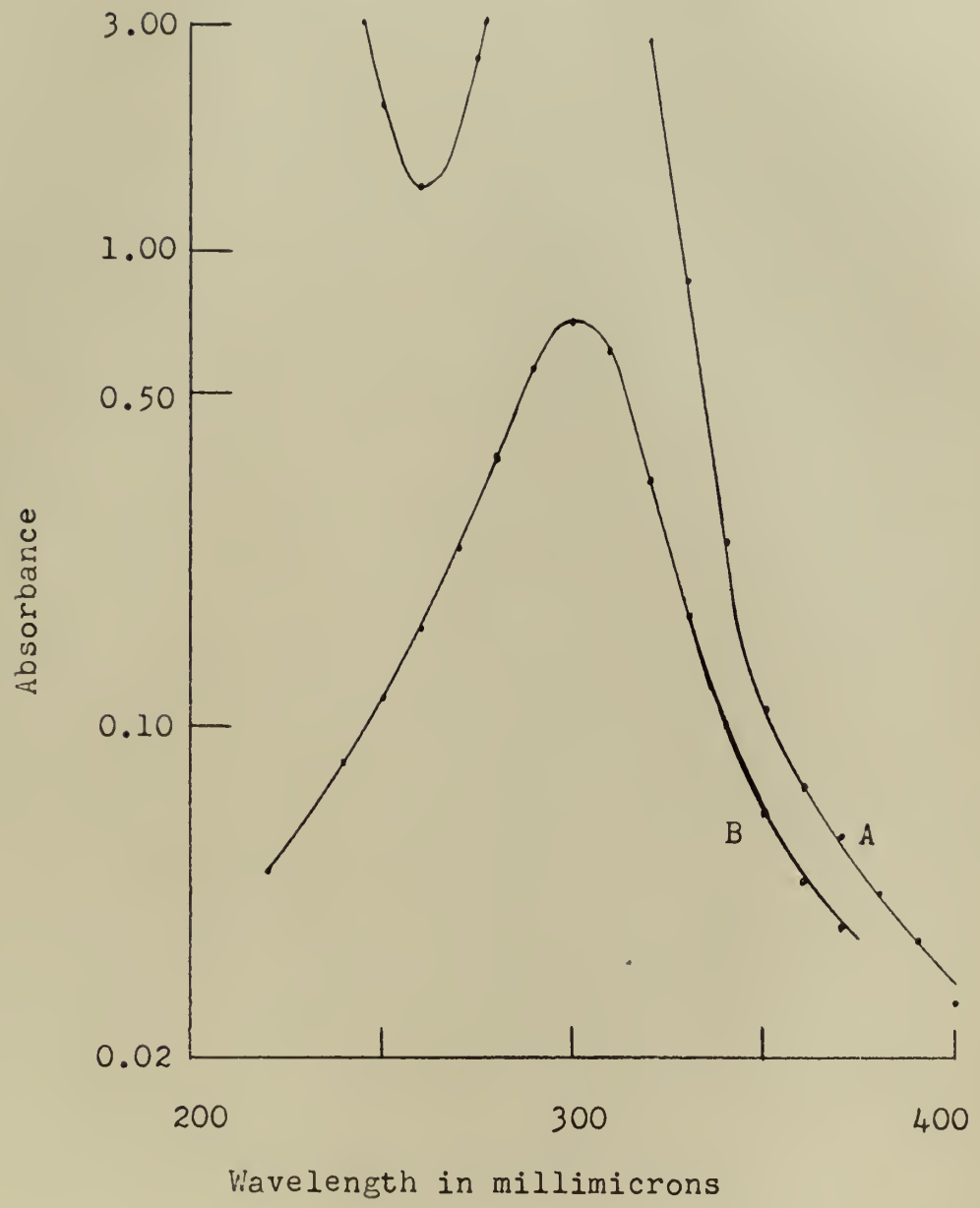
A. 4.926×10^{-3} M $Pd(NH_3)_4^{++}$ prepared by equations 1, 2 and 3

B. Solution (A) acidified with excess HCl until crystals of $Pd(NH_3)_2Cl_2$ appeared

C. Saturated solution of $Pd(NH_3)_2Cl_2$ crystals dissolved in distilled water

Figure 2

Absorbance vs Wavelength



A. $Pd(NH_3)_4^{++}$ Stock Solution

B. 9.867×10^{-2} N HNO_3 Solution

B. pH Measurements

A total of 23 runs were conducted by pH measurements, of which five were discarded because of instrumental difficulties and three were discarded for human errors. Seven runs were conducted on the system of $Pd(NH_3)_4(NO_3)_2$ plus hydrogen ion and chloride ion before it was realized that it is possible to also prepare $Pd(NH_3)_2(NO_3)_2$ in this manner [11]. Thus, the possibility existed of producing $Pd(NH_3)_2(NO_3)_2$ and/or $Pd(NH_3)_2Cl_2$ during the course of the reaction, and therefore, the remainder of the runs were conducted on the preparation of $Pd(NH_3)_2(NO_3)_2$ by

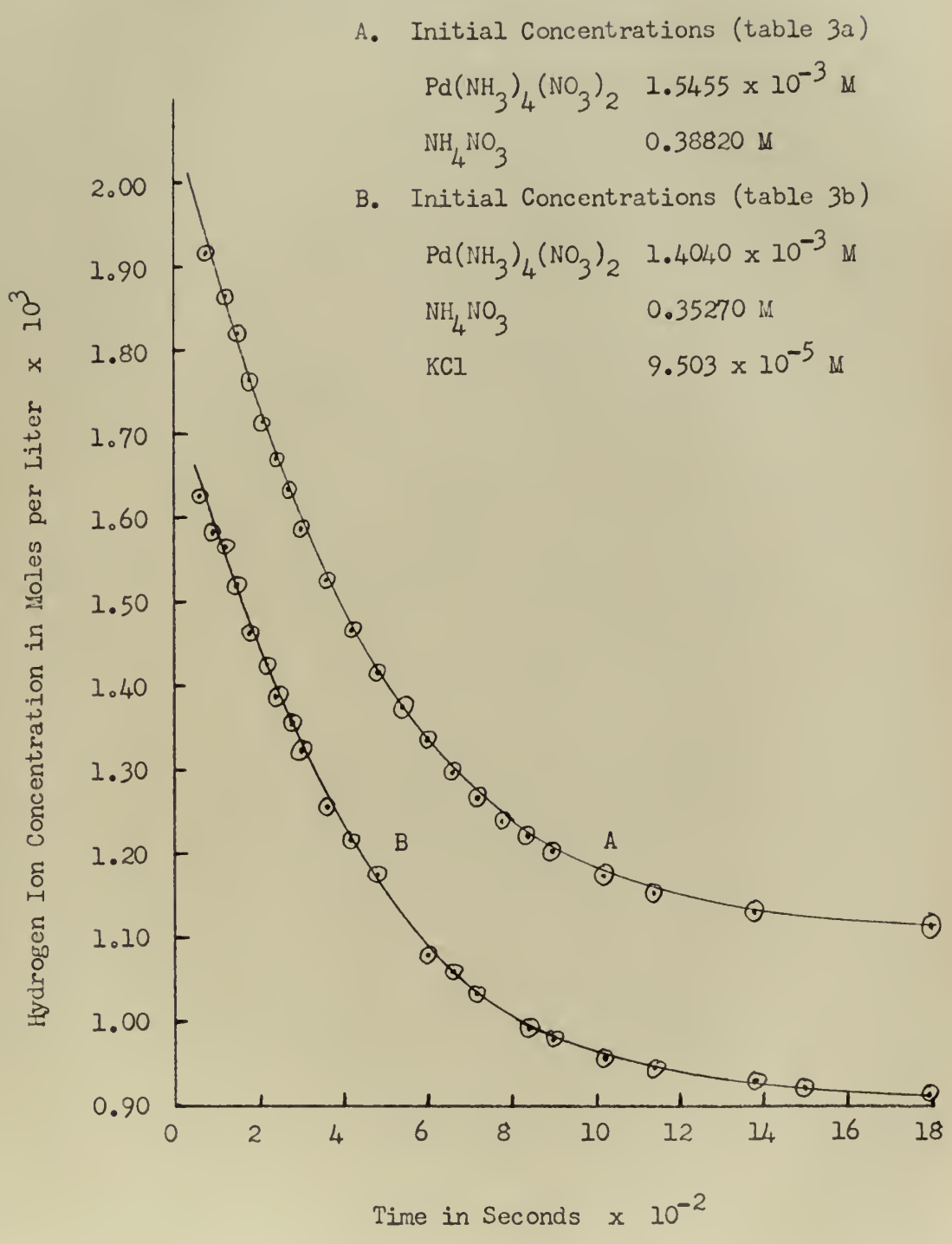
$$Pd(NH_3)_4^{++} + 2\ H^+ + 2\ NO_3^- = Pd(NH_3)_2(NO_3)_2 + 2\ NH_4^+ \qquad (9)$$

Throughout all of these runs the hydrogen ion concentration dropped at a slowly decreasing rate from t = 0 to t > 1500 seconds (curve A, fig. 3). One set of runs (#11 and #13) conducted with a very low chloride ion concentration behaved almost identically with those without the chloride ion and is also included (curve B, fig. 3). The data for all the runs on $Pd(NH_3)_2(NO_3)_2$ are presented in the appendix (table 3). Examination of table 3 shows a small difference in the hydrogen ion concentration at t = 60 seconds for two identically conducted runs; runs #11 and #13 in table 3b are an example. This difference resulted from a variation in the time of starting the clock, which was when the pipette bulb was approximately half empty. Thus a few seconds difference in timing of two similar runs was very possible.

Since the overall reaction is a double substitution, the logical choice is a mechanism with consecutive reactions of the type

Figure 3

Hydrogen Ion Concentration vs Time



$$A + B \xrightarrow{k_1} C + D \tag{10}$$

$$B + C \xrightarrow{k_2} E + D \tag{11}$$

The general form of this results in a differential equation for which there is no elementary solution. However, when $k_1 \gg k_2$ the first step is essentially complete before the second starts, so that each phase of the reaction can be treated separately as a simple second order reaction. The integrated form of the rate law for a single step reaction (such as eq. 10) is

$$k_1 t = \frac{2.303}{B_o - A_o} \log \frac{A_o B}{B_o A} \tag{12}$$

where $A = A_o - B_o + B$

For equation 9, one possibility for the first step of the substitution is

$$Pd(NH_3)_4^{++} + H^+ + NO_3^- = Pd(NH_3)_3(NO_3)^+ + NH_4^+ \tag{13}$$

Since the concentration of nitrate ion in these studies was essentially constant during the course of the reaction, the above rate law could properly be applied to this single step (eq. 13). Thus

$$k_1' t = \frac{2.303}{[H^+]_o - [Pd(NH_3)_4^{++}]_o} \log \frac{[Pd(NH_3)_4^{++}]_o [H^+]}{[H^+]_o [Pd(NH_3)_4^{++}]} \tag{14}$$

where $k_1' = k_1 f([NO_3^-])$

Similar equations apply to the second step of the substitution.

In runs #16 and #21, conducted by the isolation technique with the hydrogen ion as the limiting reactant, $[H^+]_2 - [H^+]_4$ was less than $[Pd(NH_3)_4^{++}]_o$, which means that in these runs the majority of the reaction involved only the first substitution. Applying equation 12 to these runs resulted in reasonably constant values of k_1' for a particular set of point-by-point calculations. However, the value of k_1' varied from 1.2 to 25 $\frac{\text{liter}}{\text{mole sec.}}$ depending on the value of $[H^+]_o$ used in the calculation. Extrapolation for the effective initial concentration of hydrogen ion was very difficult and of doubtful accuracy for this set of runs because most of the change in the concentration of hydrogen ion was complete within four to five minutes. This resulted in a curve of $[H^+]$ vs time with a large initial slope which in turn led to a wide range of extrapolated values of $[H^+]_o$.

Analysis of the above set of runs brought to light a discrepancy in these runs, which was that the effective initial hydrogen ion concentration ($[H^+]_2$) could not accurately be predicted beforehand. The cause of this discrepancy was the inaccuracy of the measured value of the pH of the $Pd(NH_3)_4(NO_3)_2$ stock solution, which resulted in inaccurate values for the initial ammonia concentration ($[NH_3]_o$). This in turn resulted in inaccurate values of $[H^+]_2$. For example, an increase of 0.02 pH units of the measured value of the $Pd(NH_3)_4(NO_3)_2$ stock solution would result in a 33% decrease in $[H^+]_2$ for runs #16 and #21. This particular effect appeared in all of the runs, but to a much lesser extent in the others.

The best estimate from graphical analysis of runs #16 and #21 is that k_1' is approximately 15-20 $\frac{\text{liter}}{\text{mole sec.}}$. To test this estimate, the hydrogen ion concentration at $t = 60$ seconds of runs #8, 9, 11, 12 and 20, in which the observed hydrogen ion concentration at $t = 60$ seconds was greater than $[H^+]_3$, was calculated from

$$k_1' t = \frac{2.303}{B_o - A_o} \log \frac{A_o B}{B_o A} \qquad (15)$$

where: $k_1' = 20 \frac{\text{liter}}{\text{mole sec.}}$

$B_o = [H^+]_2$ (from table 1)

$A_o = [Pd(NH_3)_4^{++}]_o$ (from table 2)

These particular runs were chosen because the observed change in hydrogen ion concentration by $t = 60$ seconds was less than that required for completion of the first substitution. Therefore, the second step was assumed to have progressed to a negligible degree and thus would not complicate the calculation. These values are presented in table 1.

The calculated values agree reasonably with the observed values and therefore the approximate value of k_1' is in accord with the observations. This value of k_1' indicates that the majority of the first substitution is completed prior to the first pH readings taken of the reaction solution in the other runs. Therefore, it is reasonable to assume that $k_1 >> k_2$, and that it is possible to calculate k_2' also from a simple single step rate law. Applying the rate equation of the second substitution (similar to eq. 14) to the data, using extrapolated

Table 1

Run	$[H^+]_1$	$[H^+]_2$	$[H^+]_3$	$[H^+]_{60}$(obs)	$[H^+]_{60}$(calc)[1]
8	4.9335 C	3.289 C	1.643 C	1.976 C	1.904 C
9	4.9335	3.289	1.643	1.970	1.904
11	4.482	2.895	1.491	1.628	1.622
13	4.482	2.895	1.491	1.596	1.622
14	4.9335	4.061	3.258	3.0254	
20	2.4667	1.595	0.822	0.895	0.929
22	9.867	8.122	6.576	6.109	
23	9.867	8.122	6.576	5.922	

1. Calculated by equation 15

values of $[H^+]_0$ from curves of $[H^+]$ vs time, resulted in a reasonably constant value of k_2' for each set of runs (table 2). These values are consistent with the previous assumption that $k_1 >> k_2$. (The values of k_2' presented in table 2 are the average value for the first 600 seconds of the runs. After 600 seconds the individual values of k_2' began to decrease slowly, apparently as equilibrium was approached. See fig. 4 and table 3.) However, comparison of values of k_2'(avg.) for different sets of runs at the same initial concentration of $Pd(NH_3)_4^{++}$ showed a small but definite difference.

Examination of table 1 shows that in runs #14, 22 and 23 the $[H^+]_{60}$(obs.) is less than $[H^+]_3$, which indicates that most of the first and part of the second substitutions have occurred; whereas in the remaining runs the substitutions have not progressed as far. Since the hydrogen ion concentration at t = 60 seconds corresponds to different degrees of progress of the first and second step of the reaction, the observed values of k_2', calculated by using graphically extrapolated values of $[H^+]_0$ (table 2), will show a slight variation for several runs at the same initial concentration of $Pd(NH_3)_4^{++}$, but at different values of $[H^+]_1$. The more hydrogen ion that was consumed reacting with $Pd(NH_3)_4^{++}$ from t = 0 to t = 60 seconds, the lower will be the observed value of k_2'. For example, $[H^+]_2 - [H^+]_{60}$(obs.) is greater in runs #22 and #23 than it is in runs #8 and #9, and k_2'(avg.) is lower for runs #22 and #23. Thus, the variation of the observed values of k_2'(avg.) for the same initial $Pd(NH_3)_4^{++}$ concentration is at least qualitatively accounted for.

Table 2

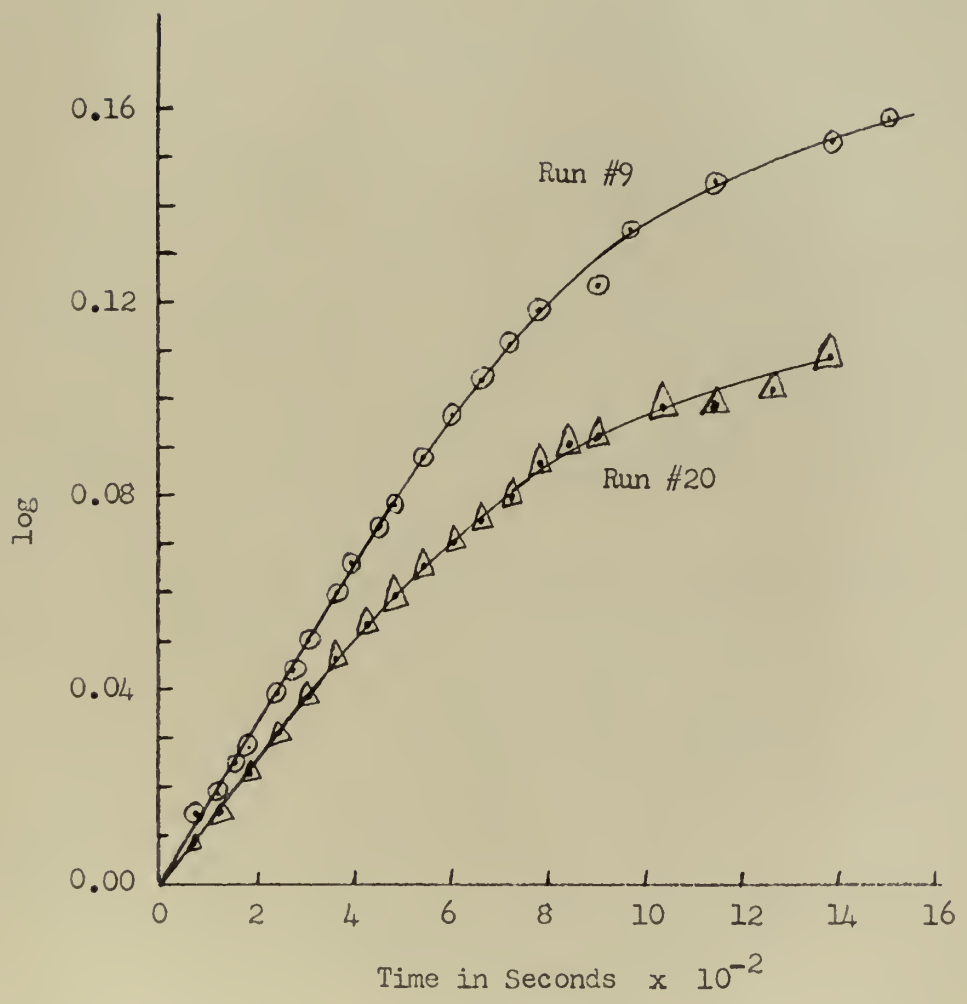
Run	$[Pd(NH_3)_4^{++}]_o$	k_2'(avg)	$[NH_4^+]$ (avg)	$[NO_3^-]$ (avg)
8	1.546 M	0.706 $\frac{\text{liter}}{\text{mole sec.}}$	0.3901 M	0.3886 M
9	1.546	0.692	0.3901	0.3886
11	1.404	0.717	0.3545	0.3537
13	1.404	0.741	0.3545	0.3537
14	0.7728	1.25	0.1954	0.1942
20	0.7728	1.59	0.1951	0.1944
22	1.546	0.238	0.3908	0.3896
23	1.546	0.199	0.3908	0.3896

$$[NH_4^+] \text{ (avg)} = [NH_4NO_3]_o + \frac{[H^+]_1 - [H^+]_4}{2}$$

$$[NO_3^-] \text{ (avg)} = [NH_4NO_3]_o + 2[Pd(NH_3)_4^{++}]_o - \frac{[H^+]_2 - [H^+]_4}{2}$$

Figure 4

$$\log \frac{[Pd(NH_3)_4^{++}]_0 \, [H^+]}{[H^+]_0 \, [Pd(NH_3)_4^{++}]} \text{ vs Time}$$



From equation 14

$$k' = k\, f([NO_3^-])$$

Comparing runs #8, 9, 11 and 13 with runs #14 and 20 shows k_2' for the first group to be approximately half of the value for the second group. In order to account for a lower value of k_2' at a higher salt concentration, it appears that k_2' must be equal to one of the following

$$\frac{k_2}{[NO_3^-]}, \quad \frac{k_2}{[NH_4^+]} \quad \text{or} \quad \frac{k_2[NO_3^-]}{[NH_4^+]^2}$$

inasmuch as $[NH_4^+] \approx [NO_3^-]$ throughout. (No experimental runs were conducted with varying ammonium or nitrate ion.) All of these forms indicate that an equilibrium is involved somewhere in the mechanism prior to the rate-determining step. However, insufficient information was available from these studies to arrive at any conclusions concerning the mechanism.

The evidence collected in these studies indicates the following forms of the rate laws; for

$$Pd(NH_3)_4^{++} + H^+ + Y = Pd(NH_3)_3(Y)^{++} + NH_4^+ \tag{16}$$

$$-\frac{d[H^+]}{dt} = k_1 \frac{[Pd(NH_3)_4^{++}][H^+]}{[X]}$$

where k_1 is approximately 3-4 second^{-1}

and for

$$Pd(NH_3)_3(Y)^{++} + H^+ + Y = Pd(NH_3)_2(Y)_2^{++} + NH_4^+ \tag{17}$$

$$-\frac{d[H^+]}{dt} = k_2 \frac{[Pd(NH_3)_3(Y)^{++}][H^+]}{[X]}$$

where k_2 is approximately 0.2 second^{-1}

C. Equilibrium Relations

Since an approach to equilibrium is indicated by the trend of the individual values of k_2' (table 3), approximate values for the possible equilibria

$$Pd(NH_3)_4^{++} + H^+ + Y \xrightleftharpoons{K_1} Pd(NH_3)_3(Y)^{++} + NH_4^+ \qquad (16)$$

$$Pd(NH_3)_3(Y)^{++} + H^+ + Y \xrightleftharpoons{K_2} Pd(NH_3)_2(Y)_2^{++} + NH_4^+ \qquad (17)$$

where $Y = H_2O$ or NO_3^-

were calculated.

Runs #16 and #21 involved primarily only the first substitution and therefore only the first equilibrium was assumed to be applicable. Hydrogen ion concentrations were extrapolated to $t = \infty$ by plotting $[H^+]$ vs $(\text{time})^{-1}$ (see fig. 5). The other concentrations were found from:

$$\left[Pd(NH_3)_4^{++}\right]_\infty = \left[Pd(NH_3)_4^{++}\right]_0 - \left(\left[H^+\right]_2 - \left[H^+\right]_\infty\right) \qquad (18)$$

$$\left[Pd(NH_3)_3(Y)^{++}\right]_\infty = \left[H^+\right]_2 - \left[H^+\right]_\infty \qquad (19)$$

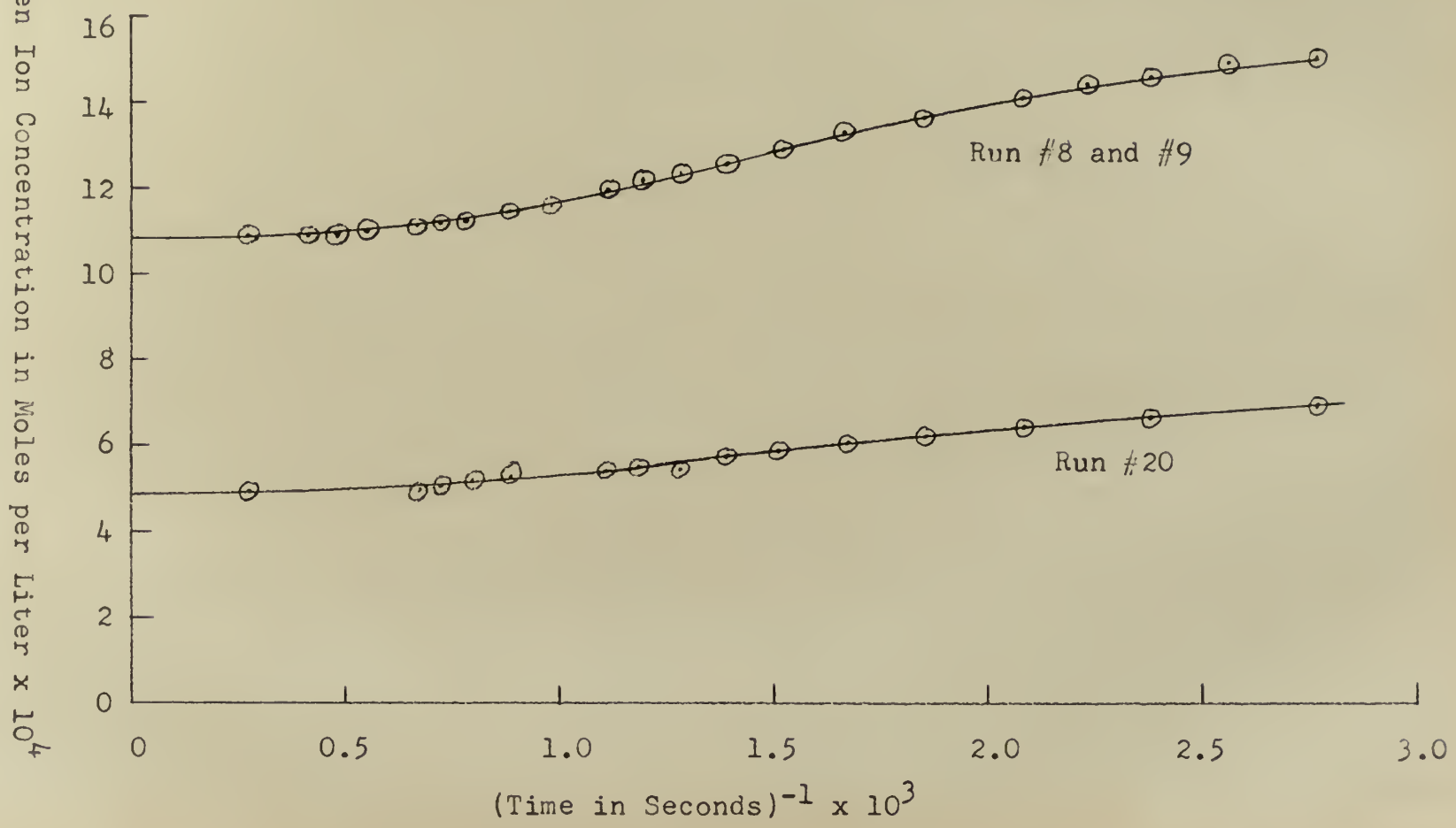
$$\left[NH_4^+\right] = \left[NH_4^+\right](\text{avg.})$$

$$\left[H^+\right]_\infty = 8.8 \times 10^{-7}\ M$$

From these, K_1 was calculated to be 4.6×10^6 when Y was assumed to be water and 2.4×10^7 when Y was assumed to be nitrate ion. Of the other runs, only #8, 9, and 20 could reasonably be extrapolated to $t = \infty$. For these runs only the second equilibrium was assumed to be applicable.

Figure 5

Hydrogen Ion Concentration vs Reciprocal Time



The concentrations were found from:

$$\left[Pd(NH_3)_3(Y)^{++}\right]_0 = \left[Pd(NH_3)_4^{++}\right]_0 \text{ (assumed)} \tag{21}$$

$$\left[Pd(NH_3)_3(Y)^{++}\right]_\infty = \left[Pd(NH_3)_3(Y)^{++}\right]_0 - \left(\left[H^+\right]_3 - \left[H^+\right]_\infty\right) \tag{22}$$

$$\left[Pd(NH_3)_2(Y)_2^{+}\right]_\infty = \left[H^+\right]_3 - \left[H^+\right]_\infty \tag{23}$$

$$\left[NH_4^+\right] = \left[NH_4^+\right] \text{(avg.)} \quad \text{(from table 2)}$$

$\left[H^+\right]_\infty$: Runs #8 and #9 1.08×10^{-3} M

Run #20 4.80×10^{-4} M

From these K_2 was calculated to be 2.1×10^4 and 3.2×10^4 when Y was assumed to be water, and 5.4×10^4 and 1.6×10^5 when Y was assumed to be nitrate ion.

These values are only approximate, but they at least indicate the relative orders of magnitude of the equilibrium constants involved.

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Table 3a

Initial Concentrations (C = mM)

$Pd(NH_3)_4(NO_3)_2$ 1.5455 C

NH_4NO_3 0.38820 M

time	Run #8		Run #9	
seconds	H^+ (±0.20 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$	H^+ (±0.20 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$
0*	2.0930 C	-----	2.0865 C	-----
60	1.9758	0.666	------	-----
75	------	-----	1.9168	0.766
90	1.9257	0.655	------	-----
120	1.8711	0.648	1.8667	0.639
150	1.8137	0.702	1.8208	0.639
180	1.7650	0.689	1.7650	0.664
210	------	-----	1.7149	0.689
240	1.6649	0.737	1.6701	0.700
270	1.6202	0.724	1.6405	0.686
300	1.5806	0.742	1.5890	0.709
330	1.5523	0.740	1.5535	0.709
360	1.5224	0.725	1.5246	0.709
390	1.4849	0.726	1.4919	0.721
420	1.4620	0.726	------	-----
450	1.4349	0.722	1.4405	0.700
480	1.4128	0.713	1.4161	0.649
510	1.3888	0.716	------	-----
540	1.3620	0.713	1.3727	0.693

Table 3a (cont'd)

time	Run #8		Run #9	
seconds	H^+	k'	H^+	k'
570	1.3398 C	-----	------ C	-----
600	1.3234	0.702	1.3327	0.687
660	1.2878	0.688	1.2968	0.668
720	1.2581	0.678	1.2669	0.653
780	1.2310	0.669	1.2396	0.642
840	------	-----	1.2214	0.591
900	1.1812	0.650	1.2026	0.581
960	1.1711	-----	------	-----
1020	1.1603	0.602	1.1730	0.578
1080	1.1539	-----	------	-----
1140	1.1441	-----	1.1522	0.541
1200	------	-----	------	-----
1260	1.1229	0.531	------	-----
1320	1.1206	-----	------	-----
1380	1.1177	-----	1.1291	0.471
1440	1.1160	-----	------	-----
1500	1.1134	0.454	------	-----
1800	1.1022	-----	1.1117	-----
2100	1.0988	-----	------	-----
2400	1.0996	-----	------	-----
3600	1.0996	-----	1.1117	-----

Table 3b

Initial Concentrations (C = mM)

$Pd(NH_3)_4(NO_3)_2$	1.404
NH_4NO_3	0.3527M
KCl	9.50×10^{-5} M

time	Run #11		Run #13	
seconds	H^+(±0.30 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$	H^+(±0.30 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$
0*	1.7221 C	-----	1.6916 C	-----
60	1.6283	0.785	1.5957	0.666
90	1.5820	0.683	1.5528	0.800
120	1.5661	0.574	1.5111	0.666
150	1.5205	0.628	1.4636	0.640
180	1.4624	0.724	1.4243	0.755
210	1.4276	0.689	1.3785	0.761
240	1.3871	0.724	1.3435	0.783
270	1.3540	0.750	1.2932	0.772
300	1.3207	0.760	1.2812	0.786
360	1.2546	0.765	1.2247	0.767
420	1.2142	0.741	1.1788	0.752
480	1.1753	0.724	1.1242	0.783
540	1.1216	0.750	1.1016	0.741
600	1.0796	0.748	1.0796	0.708
660	1.0613	0.724	1.0465	0.703
720	1.0328	0.715	1.0256	0.672

Table 3b (cont'd)

time	Run #11		Run #13	
seconds	H^+	k'	H^+	k'
780	------ C	-----	1.0058 C	0.663
840	0.9902	0.581	0.9988	0.628
900	0.9795	0.655	0.9772	0.600
1020	0.9552	-----	0.9606	-----
1140	0.9465	-----	0.9458	-----
1260	0.9341	-----	0.9312	-----
1380	0.9298	-----	0.9247	-----
1500	0.9211	-----	0.9197	-----
1800	0.9105	0.382	0.9105	0.380

Table 3c

Initial Concentrations (C = mM)

$Pd(NH_3)_4(NO_3)_2$	0.7728 C
NH_4NO_3	0.1941 M

Run #14

time seconds	H^+ (±0.10 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$
0*	3.2072 C	-----
60	3.0254	1.418
90	2.9235	1.650
120	2.8783	1.521
150	2.8471	1.396
180	2.8361	1.206
210	2.8010	1.186
240	2.7556	1.243
270	2.7279	1.223
300	2.7130	1.164
360	2.6774	1.100
420	2.6442	1.083
480	2.6115	1.082
540	2.5812	1.096
600	2.5592	1.090
660	2.5197	1.222
720	2.5080	1.198
780	2.4866	1.285

Table 3c (cont'd)

time	Run #14	
seconds	H^+	k'
840	2.4673 C	1.225
900	2.4462	1.410
1020	2.3972	-----
1140	2.3880	-----
1260	2.3620	-----
1380	2.2968	-----
1500	2.3147	-----
1800	2.2807	-----
2700	2.2178	-----

Table 3d

Initial Concentrations (C = mM)

$Pd(NH_3)_4(NO_3)_2$	7.728 C
NH_4NO_3	0.1441 M

time	Run #20	
seconds	H^+ (±2.0 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$
0*	9.5758 C	-----
60	8.9498	1.553
90	8.6686	1.413
120	8.4030	1.505
150	8.1707	1.494
180	7.9204	1.557
210	7.6775	1.555
240	7.4422	1.583
270	7.2062	1.730
300	7.0420	1.598
330	6.8795	1.625
360	6.7470	1.590
420	6.4592	1.600
480	6.2564	1.538
540	6.0600	1.513
600	5.8879	1.452
660	5.7520	1.404
720	5.6149	1.376

Table 3d (cont'd)

time	Run #20	
seconds	H^+	k'
780	5.4428 C	1.390
840	5.3505	1.350
900	5.3421	1.266
1140	5.1462	-----
1260	5.0944	-----
1380	4.9574	-----
1500	4.9962	0.884
3600	5.0549	-----

Table 3a

Initial Concentrations (C = mM)

$Pd(NH_3)_4(NO_3)_2$ 1.5455 C

NH_4NO_3 0.38820 M

time	Run #22		Run #23	
seconds	H^+ (±0.15 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$	H^+ (±0.15 C)	k' $\frac{\text{liter}}{\text{mole sec.}}$
0*	6.175 C	-----	6.2431 C	-----
60	5.1093	0.013	5.9220	0.337
90	5.7729	0.265	5.7989	0.325
120	5.7182	0.215	5.9312	0.270
150	5.5430	0.294	5.9267	0.231
180	5.7405	0.261	5.8898	0.240
210	5.6694	0.268	------	-----
240	5.7005	0.219	5.7989	0.235
270	5.6960	0.208	5.7809	0.221
300	5.6783	0.190	5.7405	0.212
330	5.6871	0.165	5.7138	0.214
360	5.5516	0.218	5.7093	0.197
420	5.5645	0.180	5.6255	0.205
480	5.4786	0.195	5.5240	0.210
540	5.5516	0.143	------	-----
600	5.5559	0.130	5.4616	0.203
660	5.4956	-----	5.4234	0.198
720	5.4757	0.129	5.3609	-----

Table 3e (cont'd)

time	Run #22		Run #23	
seconds	H^+	k'	H^+	k'
780	5.4404 C	-----	5.3436 C	0.195
840	5.3690	-----	5.3065	-----
900	5.3398	0.176	5.2613	0.198
960	5.3107	-----	------	-----
1020	5.2818	-----	5.1962	-----
1140	5.2531	-----	5.1239	-----
1260	5.2326	0.120	5.0763	0.203
1380	5.1881	-----	5.0653	-----
1500	5.1639	-----	4.9630	0.182
1800	5.0921	0.110	------	-----
2100	5.0212	-----	------	-----
2400	4.9707	-----	------	-----
2700	4.9283	0.105	4.7476	-----
3000	4.9598	-----	------	-----
6000	4.6743	-----	------	-----

Table 3F

Initial Concentrations

$Pd(NH_3)_4(NO_3)_2$	$7.7[illegible] \times 10^{-4}$ M
NH_4NO_3	0.1[illegible]1 M

time	Run #16	Run #21
seconds	H^+ ($\pm 1.5 \times 10^{-7}$)	H^+ ($\pm 1.[illegible] \times 10^{-7}$)
0*	11.487×10^{-7} M	$11.17[illegible] \times 10^{-7}$ M
60	10.948	10.636
90	10.479	10.317
120	10.174	10.087
150	9.9857	10.024
180	9.8647	9.9326
210	9.7704	9.8466
240	9.7250	9.7856
270	------	9.7400
300	9.6046	------
330	9.5302	9.7022
360	9.5302	9.6796
420	9.5078	9.6270
480	9.4932	------
540	------	9.5448
600	9.5078	9.5598
660	9.2740	------
720	9.2194	9.5896

Table 3f (cont'd)

time seconds	Run #16 H^+	Run #21 H^+
780	9.2886×10^{-7} M	9.5448×10^{-7} M
840	9.2812	9.5078
900	9.3030	9.5210
1200	9.2308	9.2956
1500	9.2194	9.0458
1800	8.9312	------
3000	8.8440	------
3600	------	8.7004
5000	------	8.2458

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